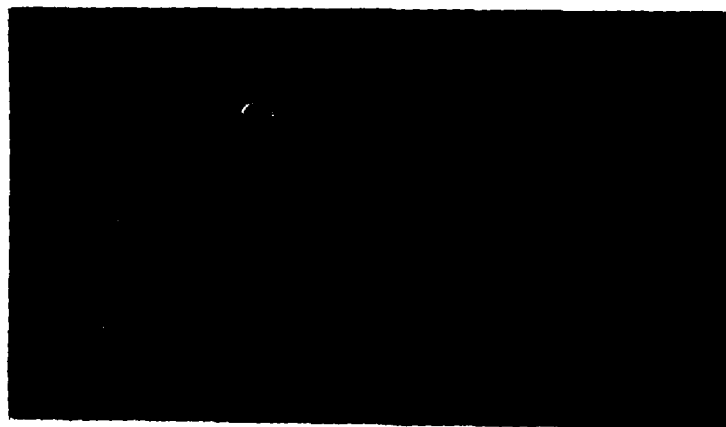


NOT FOR COPY

4



AD-A205 555

DTIC  
ELECTE  
MAR 13 1989  
S  
WD



*UNIVERSITY of PENNSYLVANIA*

PHILADELPHIA, PENNSYLVANIA 19104

DISTRIBUTION STATEMENT A

Approved for public release  
Distribution Unlimited

89 2 24 051

④

NINTH QUARTERLY R&D STATUS REPORT

Principal Investigator:  
Alan G. MacDiarmid  
Department of Chemistry  
University of Pennsylvania

REPORTING PERIOD: 10/1/88 - 12/31/88

ARPA ORDER NO.: a400004df301  
PROGRAM CODE NO.: 6103

CONTRACTOR: Trustees of the University of Pennsylvania  
Office of Research Administration  
Suite 300 Mellon Building  
133 S. 36th Street  
Philadelphia, PA 19104-3246

CONTRACT NO.: N00014-86-K-0766

CONTRACT AMOUNT: \$9,420,613

EFFECTIVE DATE  
OF CONTRACT: 9/15/86

EXPIRATION DATE  
OF CONTRACT: 9/14/91

TELEPHONE NO.: 215-898-8307 or 215-898-6323

SHORT TITLE OF WORK: Conducting Electronic Polymers by  
Non-Redox Processes

DTIC  
SELECTED  
MAR 13 1989  
S D

DISTRIBUTION STATEMENT A  
Approved for public release  
Distribution is unlimited

## Table of Contents

I.	Research Groups	1
II.	Description of Progress	2
	1. University of Pennsylvania	2
	2. The Ohio State University	4
	3. Lockheed Advanced Aeronautics Corporation	9
	4. Rensselaer Polytechnic Institute	11
	5. University of Rhode Island	12
	6. Montclair State College	13
III.	Working Relationships Involving University of Pennsylvania Personnel and Those of the Subcontractors	13
IV.	Miscellaneous Scientific Interactions of Key Personnel Associated with the Program	14
V.	Publications	16
	Published Papers	16
	Papers accepted/submitted for publication	17
VI.	Patents	18
VII.	Changes in Personnel	18
	1. University of Pennsylvania	18
	2. The Ohio State University	18
	3. Lockheed Advanced Aeronautics Corporation	19
	4. Rensselaer Polytechnic Institute	19
	5. University of Rhode Island	19

6. Montclair State College	19
VIII. Hiring of New Faculty from URI Funds	19
IX. Contractual Administration	21
X. Fiscal Status	22



per call JC

A-1

## I. Research Groups\*

1. University of Pennsylvania
  - (a) Department of Chemistry (A.G. MacDiarmid)
  - (b) Department of Materials Science (G.C. Farrington)
2. The Ohio State University  
Department of Physics (A.J. Epstein)
3. Lockheed Advanced Aeronautics Corporation  
Aeronautics Systems Group Research (T.S. Kuan)
4. Rensselaer Polytechnic Institute  
Department of Chemistry (G.E. Wnek)
5. University of Rhode Island  
Department of Chemistry (S.C. Yang)
6. Montclair State College  
Department of Chemistry (B.D. Humphrey)

\*Financial information for each group given in Section X.

## II. Description of Progress

### 1. University of Pennsylvania

#### a. Department of Chemistry (MacDiarmid)†

##### (i) Summary of Progress

#### Highly Conducting Polyacetylene: Possible Dependency of Conductivity on Chemical Composition\*

The chemical composition and the IR spectra of both the "New" and "ARA" undoped forms of BASF  $(CH)_x$  either oriented, or non-oriented have been examined. Even after extensive washing (up to 5 days) and/or after treatment with  $CH_3OH/HCl$ , relatively large amounts (up to ~5%) of Ti, Al and Si residues remain in the film. This is consistent with their infrared spectra, which show strong vibrations characteristic of  $sp^3$ -hybridized carbon believed to be associated primarily with the  $Ti(n-OBu)_4$  catalyst. The conductivity of the  $I_2/CCl_4$ -doped films varies greatly from one portion of a film to another. For example, a non-oriented doped ARA film (elemental analysis: residue ~4.6%; exhibited ( $\sigma$  15 determinations) a  $\sigma$  (max) ~8100,  $\sigma$  (min) 500,  $\sigma$  (av) 940,  $\sigma$  (median) 880 S/cm. It is therefore suggested that the residual catalyst in the film possibly acts as a "pre-dopant" and that more complete removal of catalyst residues will substantially change the conductivity.

\*Work supported in part by URI and in part by NSF Grant No. DMR-85-19059.

#### In Situ Adsorption-Polymerization of Anilines and Pyrrole\*

Strongly-adhering, transparent, cohesive films (~0.1  $\mu m$ ) of polyaniline (emeraldine•HCl) and also its N-substituted derivatives can be deposited on a variety of substrates such as glass, nylon, metals, AgCl pellets, etc. from aqueous solutions of the corresponding anilines, HCl and  $(NH_4)_2S_2O_8$  during the initial stages of polymerization. They can also be deposited on polypyrrole films formed in a similar manner. It is proposed that a reactive, soluble, intermediate species is adsorbed on the surface of the substrate where it then polymerizes in situ. The films undergo chemical reaction, e.g. oxidation/ reduction, protonation/deprotonation, alkylation, etc. without degradation. Excellent IR and vis/UV spectra as well as cyclic voltammograms can be obtained on the as-

†In collaboration with Professor A.J. Epstein, Department of Physics, The Ohio State University.

formed or chemically modified films thus providing an easy, rapid and reliable method of characterization.

\*Work supported in part by URI and in part by NSF Grant No. DMR-85-19059.

#### Water Soluble Polyaniline\*

Oxidative polymerization of ortho ethoxyaniline by  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  yields a protonated polyaniline ( $\sigma \sim 10^{-2} \text{ S/cm}$ ) which is soluble in water to give a dark green solution from which films of the less protonated polymer can be cast on a variety of substrates. Complete deprotonation with  $\text{NH}_4\text{OH}$  yields a polymer, soluble in NMP from which bronze films can be cast. Its composition is consistent with that expected for the base form of polyaniline containing one -OEt group on each ring: Analysis: Found: C 71.47; H 6.45; N 10.37%; Calc.: C 71.37; H 6.32; N 10.41%. Electronic, magnetic, and optical properties have been compared with those of the corresponding ortho- $\text{CH}_3$  and ortho-Et derivatives.

\*Work supported in part by URI and in part by NSF Grant No. DMR-85-19059.

#### (ii) Major Equipment Purchased or Constructed

Miscellaneous supplies for the Lambda-9 spectrophotometer were purchased. These include 10 mm, 1 mm light path uv-vis cells and a solid state sample holder.

#### b. Department of Materials Science and Engineering (Farrington)

##### Summary of Progress

Ching-min Wu and Rokeya Huq are beginning a study of the electrochemical redox reactions of  $\text{Zn(II)}$  cations dissolved in poly(ethylene oxide) (PEO). Electrolytes of this sort were prepared initially because of their potential application in high energy density batteries using lithium anodes. However, studies suggested that the  $\text{Zn(II)}$  ions are immobile in the PEO matrix. However, it now appears that they may diffuse quite rapidly indeed. Wu and Huq are designing and constructing the necessary apparatus to carry out electrochemistry in a polymer medium from 25-200°C in an inert atmosphere.

Gary Jones continues his studies of ion/polymer binding in PEO electrolytes using dynamic mechanical analysis. In addition, he has begun exploring the role of mechanical shear, thermal treatment, and ion-catalyzed reactions on the stability of PEO. It appears that even gentle stirring of a non-aqueous solution of PEO results in chain shortening. This work is particularly important for designing procedures for preparing reproducible samples of PEO electrolytes. In addition, chain scission catalyzed by the presence of transition metal cations may explain the mysterious and dramatic increase in conductivity that PEO electrolytes containing Ni(II) ions undergo upon mild thermal treatment.

## 2. The Ohio State University

### Department of Physics (Epstein)<sup>‡</sup>

#### (i) Summary of Progress

We report a new technique to produce oriented, crystalline polyaniline films using simultaneous heat treatment and stressing of emeraldine base films. Samples were observed to elongate by 250% when held at elevated temperatures ( $T \geq 110^\circ\text{C}$ ), and showed anisotropic x-ray and IR response. IR interference data on thin films indicate an anisotropy in the index of refraction of ~20% for parallel and perpendicular polarizations, and x-ray studies show a directional enhancement in the Debye-Scherrer rings. Up to two orders of magnitude increase of conductivity of the oriented salt obtained by HCl treatment of the oriented base is observed.

We have extended our detailed x-ray diffraction studies of emeraldine form of polyaniline. We have distinguished two distinct structural families of emeraldine. This is the first systematic detailed observation of competing crystalline phases in a doped polymer. The multiple structures of the emeraldine form of polyaniline, together with their preparation methods, correlate with dramatic differences in the stable electronic structures corresponding to the formation of polaronic energy bands or charged spinless defects. Specific structures are proposed for the different phases and their correlation with the known electronic states and other properties has been determined.

Class I of the emeraldine form of polyaniline consists of materials prepared in the conducting, doped (salt, ES) form. They form substantially

<sup>‡</sup>In collaboration with Professor A.G. MacDiarmid, Department of Chemistry, University of Pennsylvania.



crystalline salts ES-I. Dedoping leads to an amorphous insulating base, EB-I. Class II consists of materials prepared in the base form, EB-II, which is up to 50% crystalline. Initial doping occurs in the amorphous region forming ES-II. At higher doping, the crystalline component dopes to a new ES-II structure.

There is a striking difference in behavior for  $\chi^P$  vs.  $x$  for doping into EB-I and EB-II. *The nearly linear increase in  $\chi^P$  with  $x$  for ES-I correlates well with the increased growth of structure ES-I with protonation. On the other hand, the  $\chi^P$  for doping into EB-II with  $x < 0.25$  is essentially zero, with a dramatic increase in  $\chi^P$  as  $x$  exceeds 0.25.* This is in accord with the results of diffraction which show doping only in the amorphous phase of EB-II for  $x < 0.25$  and a corresponding change in the crystalline structure for  $x > 0.25$ . Thus, while  $\chi^P$  expected for a polaron lattice is observed when there is either crystalline ES-I or ES-II phase present, protonation into the amorphous regions of EB-II forming ES-II *leads to spinless defects*. The charge state introduced by protonation in the amorphous part of EB-II remains spinless until essentially maximum protonation achieved in the amorphous region, and then, protonation begins to proceed in crystalline regions with the onset of  $\chi^P$ . The likely charge defects within the protonated amorphous region are doubly charged bipolarons, as well as protonated amine units ( $-\text{NH}_2^+$ ). The absence of a high spin state in the amorphous region shows the inability of the polyaniline polymer to form a Fermi glass as the polaron metal becomes completely disordered, instead spinless charge defects form. The presence of small *islands* of emeraldine salt formed within either EB-I or EB-II is in accord with our earlier proposal of charge transport in the polymer being dominated by charging energy limited tunneling, and application of this granular metal model to far IR absorption.

The crystal structure parameters are summarized in the Table. The differences among the ES-I and ES-II structures can be thought of in terms of the difference in phase of the polymer zigzag and  $\text{Cl}^-$  for the two chains present in the unit cell. The presence of a "memory effect" such that upon protonation EB-I forms ES-I and not ES-II is intriguing and may reflect the presence of residual orientation between neighboring chains even after the materials were dedoped from their original ES-I form to the amorphous state (EB-I form). The two classes of structure can be qualitatively understood by the different nature of cohesion forces acting during the preparation of materials: van der Waals forces and repulsion between  $\pi$  ring orbitals for EB-II, the same forces plus Coulomb interaction for ES-I (Madelung energy is also important for ES-II, but it acts during the doping process for the placement of  $\text{Cl}^-$  in pre-existing cavities in the host lattice). It is noted that the details of the crystal structure are

Table: Emeraldine Crystal Structures

Phase	X	Space Group	a, Å	b, Å	c, Å	a <sup>(1)</sup>	V <sup>(1)</sup> Å <sup>3</sup>	F <sup>(1)</sup>	$\delta^{(1)}$	$\chi^p$
EB—I	x=0.0	amorphous	—	—	—	—	—	—	—	no
ES—I(2)	0<x<0.5	P <sub>2</sub> <sub>1</sub> monoclinic	7.0	8.6	9.6	83°	570	—	121°	yes
ES—I	0<x<0.5	amorphous	—	—	—	—	—	—	—	no
EB—II	x=0.0	P <sub>bcn</sub> , orthorhombic(3)	7.7	5.7	9.8	90°	430	~±42°	125°	no
ES—II(4)	x>0.25	P <sub>2</sub> <sub>1</sub> 2 <sub>2</sub> 1, orthorhombic	7.0	8.6	10.05	90°	600	~±47°	131°	yes
ES—II	0<x<0.25	amorphous	—	—	—	—	—	—	—	no

(1)a≡monoclinic angle; V≡unit cell volume; Φ≡ring tilt angle from the N—backbone plane deduced from crystal packing argument along b according to the structures proposed;  $\delta \equiv$  ring—N—ring angle calculated for N—ring—N lengths of 5.5Å

(2)Monoclinic parameters and amorphous content vary with x (the parameters given here are for x=0.5).

(3)Space group of the average structure, neglecting the ordering of benzenoid and quinoid sequences of the polymer

(4)Detailed parameters vary within a given sample.

dependent upon counterion used. In addition, the solubility of polyaniline is dependent upon its crystallinity.

We have undertaken extensive reanalysis of our picosecond photoinduced bleaching (PB) data for the exciton absorption in emeraldine base. Our results are characteristically different from those reported earlier for either polyacetylene or a-Si:H.

Different dispersive decays of the PB are observed for short times ( $t < ns$ ,  $T$  independent) and long times ( $T > 1$  ms, weakly  $T$  dependent). The variation of PB as  $t^{-\beta}$  with  $\beta \cong 0.115$  for  $20$  ps  $> t > 4$  ns rules out the usual geminate recombination process ( $\beta \cong 0.5$  on this time scale), in contrast to PB in polyacetylene. The  $T$  independence of  $\beta$  rules out the role of thermalization of photoinduced carriers via multiple trapping as, for example, in a Si:H. These results for EB support the central role of exciton formation with subsequent lattice relaxation, pointing to the importance of rotations in ring-containing polymer systems. The dispersive behavior of the PB likely reflects stochastic aspects of both spatial and temporal factors controlling recombination.

The origins of the short time recombination process and long time delays are of fundamental importance. The absence of  $t^{-0.5}$  kinetics for  $T > 40$  ps demonstrates that the recombination process is substantially different than that predicted for geminate recombination and observed for polymers such as polyacetylene. Separation of all the excited electrons and holes upon promotion of the electrons to the conduction band is ruled out by the linear intensity dependence of the near-steady state and picosecond PB of the 2eV transition, as well as by the absence of a  $T$  dependence of  $\beta$  expected for charge motion of the photoexcited electrons in a disordered conduction band as observed, for example, in a-Si:H. This  $T$ -independence of the short-time  $\beta$  is in accord with the absence of significant transient photoconductivity in EB. It is noted that some fraction of the initially excited e-h pairs results in the formation of separated positive and negative polarons ( $P^+$ ,  $P^-$ ); however, the laser intensity, temperature, and temporal dependences of the near-infrared through ultraviolet and far infrared features associated with the  $P^+$  and  $P^-$  are dramatically different than the corresponding behavior of the 2eV bleaching. Once formed, the  $P^+$  and  $P^-$  thus have little affect on the observed dynamics of the bleaching of the 2eV absorption.

During the excitation process, the Franck-Condon principle is expected to hold, so that the excited state of the system is not initially in its energetically preferred configuration. Relaxation directly from the excited state  $e^*$  to the

ground state  $g$  does not involve lattice relaxation, hence may be rapid and not thermally activated. On the other hand, relaxation from the higher energy state  $e^*$  to the more favored state  $e$  is likely to involve coordinated ring rotations that require the presence of free volume sufficient to allow rotation. Decay from the state  $e$  back to the ground state  $g$  will require thermal activation of free volume for rotation. The reported temperature dependence of long-time photoinduced polaron decays and NMR studies of the temperature dependence of ring flipping processes in emeraldine support this view. Hence, the long lived excitations which bleach the 2eV transition are likely to be an exciton state stabilized by ring rotation. The EB form of polyaniline is usually amorphous, with no more than 50% crystallinity (and x-ray coherence lengths less than 100 Å within the "crystalline" regions). As a result, the substantial disorder present in the polymer is expected to lead to dispersion in free volume activation energies (stochastic distribution of spatial properties) that is the likely origin of the difference in the recombination rates at short and long times. The weak  $T$  dependence of the long-time decay may reflect the necessity of coordinated molecular motion for ring rotations. These ring rotations processes are also expected to play an important role in the dynamics of the polarons formed in polyaniline. It is noted that charge recombination within the exciton without concomitant ring relaxation to the ground state configuration may lead to the formation of neutral defects or "conformons" that can contribute to the very long time bleaching of the exciton transition.

These extensive studies show that the important role of ring rotations in polyaniline have led us to reexamine more carefully the type of charge defect states formed in these systems. We have begun to develop a phenomenological theory to represent the small, massive polarons in terms of local distortions of the ring torsion angles. This concept should be relevant to large  $\pi$ - $\pi^*$  energy gap polymers including leucoemeraldine, emeraldine and pernigraniline as well as other ring containing polymers, such as polyparaphenylenesulfide.

In our parallel efforts to test the concepts of local charge states in low dimensional solids, we have carried out photoinduced infrared through ultraviolet absorption on  $Y_1Ba_2Cu_3O_{6+x}$ . We measured an absolute absorbance spectra which shows peaks at 0.5, 1.6, 3.0, 4.3 and 5.3 eV. Photoinduced absorption shows peaks at 1.2, 1.4 and 0.13 eV together with photoinduced bleaching at energies  $> \sim 1.6$  eV. Several photoinduced IRAV modes indicate a loss of symmetry upon photoexcitation. A new photoinduced IRAV mode at  $\sim 310$   $cm^{-1}$  and bleaching of several IR modes suggest a tetragonal to orthorhombic transition occurs upon photoexcitation, possibly associated with symmetry lowering due to a hole state resident on an oxygen site.

(ii) Major Equipment Purchased or Constructed

Miscellaneous optical components were purchased including filters, windows, lenses, and lamps. Liquid cells were purchased for solution studies. The purchase of near-IR and mid-IR polarizers will enable polarized infrared measurements on oriented samples. A mercury-xenon arc lamp was purchased to enable photoinduced IR and visible experiments using a pump beam in the range 3 to 4 eV. Because of problems with the building power supply, a power conditioner was purchased for the FTIR spectrometer to protect it from line surges. To enable reflection measurements in the FTIR spectrometer, a reflection attachment was purchased. Purchase of a liquid helium cryostat was necessary in order to continue microwave conductivity measurements. For accurate temperature measurements in the EPR spectrometer, a silicon diode thermometer was purchased.

3. Lockheed Advanced Aeronautics Corporation

Aeronautics Systems Group Research (Kuan)

Summary of Progress

During this last quarter our group has been concluding research on the mechanism of aniline oxidative polymerization. Through these studies we found that N-phenyl-p-phenylenediamine, (p-dianiline), is an intermediate of aniline polymerization. Oxidized p-dianiline is capable of reacting with unoxidized aniline to form a trimer. Further oxidation of the trimer and subsequent aniline oligomers followed by reaction with unoxidized aniline can occur until conductive polyaniline is formed. We feel this reactivity explains the "autocatalytic" polymerization of aniline witnessed by other groups.

This phenomenon reveals the possibility of having a thermosetting synthesis of polyaniline. If polyaniline can be synthesized via the reaction of p-phenylenediamine with oxidized N,N'-diphenyl-p-phenylenediamine, and these two reactants are meltable, a melt of these two reactants in the presence of an acid, such as tosylic acid, would cure to form polyaniline. Initial studies show that these two reactants do melt at 110°C and react to form a film with a much higher melting point, however the electrical conductivity of the film is very low. The film goes from blue in transmission to green, suggesting that these two reactants have reacted to form a polymer. However, either the molecular

weight of the product is very low, or excessive ortho, versus para, substitution has occurred. Further studies will be performed to determine whether a thermosetting melt of oxidized N,N'-diphenyl-p-phenylenediamine and p-phenylenediamine can be used to make conductive polyaniline.

This phenomenon also reveals the possible control of polyaniline oligomer synthesis by reacting stoichiometric amounts of aniline or p-phenylenediamine with oxidized p-dianiline or oxidized N,N'-diphenyl-p-phenylenediamine. For example, one mole of oxidized N,N'-diphenyl-p-phenylenediamine may possibly react with two moles of p-phenylenediamine to form a diamine capped tetramer. Further reactivity could lead to the formation of larger oligomers. The amine terminated polyaniline could possibly be used as a backbone segment of a polyimide. Aside from polyaniline synthesis, we have also worked on studying the nature of polyaniline blended with solid electrolytes. We have been studying a blend of tosylic acid doped polyaniline and polyethyleneoxide. We found that a 50:50 blend of tosylic acid doped polyaniline:PEO could form a homogeneous film from formic acid. Application of an electrical potential across this film formed a conductive gradient across the film. A portion of the film closest to the anode became oxidized and nonconductive while the portion of the film closest to the cathode became reduced and nonconductive. A thin strip of the film separating the oxidized and reduced segments of the film remained conductive. This was monitored visually and by making resistance measurements across the film at various distances from the electrodes. The resistance was found to vary by four orders of magnitude across the film. This phenomenon is strongly dependant on movement, the ability of polyaniline's conductivity to be decreased by oxidizing or reducing the polymer, and by an electrical resistance between the electrodes.

We have also begun groundwork to study the nature of the polyaniline/anhydride chemical bond. Initial studies suggest that anhydrides will render polyaniline emeraldine free-base electrically conductive. However, excessive binding of anhydrides to polyaniline withdraw too much electron density from the polymer backbone and decreases the conductivity of the material. We will study the interaction of anhydrides with N,N'-diphenyl-p-phenylenediamine as a model to represent polyaniline. This work will be a joint project with Alan MacDiarmid's group. Dr. MacDiarmid's group have performed studies on the interaction of protonic acids with N,N'-diphenyl-p-phenylenediamine and will be compared with our work to fully understand the interactions of Lewis acids with polyaniline emeraldine free base.

#### 4. Rensselaer Polytechnic Institute

##### Department of Chemistry (Wnek)

##### Summary of Progress

We have continued our investigation of the doping of cis-1,4-polyisoprene, PI, with iodine. Of particular importance are spectroscopic experiments using small organic molecules (2-methyl-2-butene, trans-3-hexene, and 2,3-dimethyl-2-butene) which are representative of repeating units in polybutadiene, polyisoprene, and poly(2,3-dimethylbutadiene).  $^1\text{H}$  NMR studies offer no evidence for free radical (radical cation) formation, as sharp resonance lines are observed. In the case of 2-methyl-2-butene, the spectra are consistent with addition of iodine across the double bonds (as expected), and with the addition of HI (presumably from dehydroiodination) across the double bonds (also an expected reaction). We are in the process of attempting to separate and isolate the products of these reactions in order to map out the various reaction pathways. What is clear is that the chemistry is inconsistent with initial proposals of radical cation formation upon treatment of PI with iodine.

We are wrapping up our studies on the binding of cationic proteins by polypyrrole/polystyrenesulfonate (PP/PPS) composites. Spectroscopic experiments to date indicate that the proteins remove PPS from the films upon reduction of PP. We hope to confirm and quantify this observation with quartz crystal microbalance studies being performed by Professor John Reynolds at the University of Texas at Arlington.

Finally,  $^{15}\text{N}$ -labeled polyaniline has been prepared and its structure studied by  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR spectroscopy at the University of Massachusetts by Professor James Chien and his group. (The labeled aniline was purchased using URI funds.) It was found that the NMR relaxation in emeraldine salt results from the sum of contributions from processes such as proton exchange, chlorine quadrupolar relaxation, and electronic spin-nuclear interaction. A bimodal spin lattice relaxation time for protons was found, implying two relaxationally different domains on the scale of ca.  $10\text{\AA}$ . It is likely that the faster relaxation is associated with nitrogen radical cations. An average number of aniline repeat units of 50 was estimated from the spectra.

## 5. University of Rhode Island

Department of Chemistry (Yang)

### Summary of Progress

In this quarter we made progress in two areas:

#### Polymer morphology at polyaniline/electrode interface

The interest on interfacial morphology arises from the fact that the quality of interface is important to applications in electronics and optical applications. The interfacial morphology strongly influences the properties such as: charge transfer, mechanical strength, adhesion, optical quality, and color-switching speed. These properties are important to device applications.

In this quarter we have investigated the morphology of very thin layer of polymer at various stages of electrochemical growth. Electron microscopy was used to observe the polymer-to-substrate binding at the nucleation stage, the formation of the first few layers, and the thick (1 micron) conducting polymer coatings. Our study reveals that the morphology of thin polyaniline (0.1 to 0.2 micron) is controlled by kinetic competition between polymer growth on electrode surface and the extension of conducting polymer fibers.

We have also started study on the morphology of polyaniline synthesized at different electrolysis rates. We have compared the morphology of polyaniline with potentiostatic and potential cycling preparations. We found that these techniques allow for additional control of polymer morphology.

From our experience with electrochemical control of polymer morphology, we think that it is promising for making thin film conducting polymers with molecularly aligned fibers for novel electronic and optical applications.

#### Kinetics study of thin film polyaniline

One of the purposes of making morphological modification is to improve the properties of conducting polymers as reversibly property-switchable materials. Polyaniline can be reversibly switched between conductor and insulator, among clear, green, blue and purple colors. These properties have potential applications in "smart windows", electronic information display screens and electro-optical light filters. In these applications there are differing demands for the response times of electrical or optical switchings. This study is to understand the kinetics of these property-switching processes.



In this quarter, we are setting up an apparatus for simultaneously measuring kinetic spectroscopy and electrochemistry. Kinetic spectroscopy is carried out using a fast scanning FTIR spectrometer having a time resolution of 20 milliseconds, and the electrochemistry is measured by a computer-controlled potentiostat with a time resolution of 10 microseconds. We have begun studying the interesting effect of polymer dynamics that we discovered last summer. Initial data taken are promising with regard to providing insights into the origin of the effect due to polymer dynamics.

#### 6. Montclair State College

Department of Chemistry (Humphrey)

##### Major Equipment Purchased or Constructed

During this quarter, we have purchased several pieces of scientific equipment using URI support. The major equipment purchased includes a viscosity apparatus, a turbidimeter, size exclusion chromatography columns, a data acquisition computer station, a rotating ring-disk electrode assembly and an xy recorder. The purpose of this equipment is for further characterization of the conducting polymers and composite materials being synthesized. In particular, this equipment will aid in the determination of the molecular weights and the charge transfer characteristics of the new materials synthesized. At present this equipment is still being uncrated and set up in my lab at Montclair State.

#### III. Working Relationships Involving University of Pennsylvania Personnel and Those of Subcontractors

The following interactions between personnel funded by the URI contract have taken place during this quarter:

1. October 13, 1988, Mr. Mikolaj Jozefowicz of the Ohio State University, Columbus, OH visited Dr. MacDiarmid's laboratory. Title of talk given: "Structure of Polyaniline."
2. December 13, 1988, Dr. Teh Kuan of Lockheed Corporation, Valencia, CA visited Dr. MacDiarmid's lab. Title of talk given: "Electrically Conductive Plastics - New Materials from Aerospace Research."

3. December 14, 1988, Mr. Mikolaj Jozefowicz of the Ohio State University, Columbus, OH visited Dr. MacDiarmid's laboratory. Title of talk given: "Some Details on Preparation and X-Ray Studies of Structured Polyaniline Films."

IV. Miscellaneous Scientific Interactions of Key Personnel Associated with the Program involving (i) visits to their laboratories by persons concerned with conducting polymers, (ii) visits by them to other laboratories and (iii) lectures on their research at organized symposia.

1. October 1-4, 1988, Dr. Epstein met in Orsay, France with Professor Jean-Paul Pouget at the Universite Paris-Sud, France, to perform crystal structure studies on the polyanilines (expenses paid by other sources).

2. October 4-7, 1988, Dr. Epstein attended the International Symposium on the Electronic Structure of High T<sub>c</sub> Superconductors in Rome, Italy (expenses paid by other sources).

3. October 7-8, 1988, Dr. Howard Reiss of the University of California, Irvine, CA, visited Dr. MacDiarmid's laboratory where he had discussions with Dr. MacDiarmid, Mr. Anjan Ray and Mr. Elliot Scherr.

4. October 9-14, 1988, Dr. Farrington gave an invited talk at the 174th meeting of the Electrochemical Society at Chicago, IL. Title of the talk, "Zn(II) mobility in Poly (Ethylene Oxide)."

5. October 13, 1988, Dr. John Tranquada, Brookhaven National Laboratories, Upton, NY, visited Dr. Epstein's laboratory. He met with Dr. Epstein and discussed ordering of magnetic spins in materials.

6. October 19, 1988, Dr. Michael Binder and Dr. Robert Mammone, U.S. Army Electronics Technology and Devices Laboratory, Fort Monmouth, NJ, visited Dr. Epstein's laboratory. They met and discussed with Dr. Epstein applications of conducting polymers. Title of informal lecture: "Electrochemistry of Non-Aqueous Battery Systems."

7. October 23-25, 1988, Dr. Epstein participated in the Advanced Materials Meeting at E.I. DuPont de Nemours, Wilmington, DE, which celebrated the 50th anniversary of nylon and teflon (expenses paid by other sources).

8. October 25, 1988, Dr. Yukio Kobayashi of Showa-Denko Co., Tokyo, Japan, visited Dr. MacDiarmid's laboratory where they discussed research on conducting polymers.
9. November 3-4, 1988, Dr. Epstein presented a colloquium at the Department of Physics, University of Buffalo, Buffalo, NY. Title of talk given: "Novel Electronic Phenomena" (expenses paid by other sources).
10. November 6-25, 1988, Ms. Christine Menardo of the University of Grenoble, France, visited Dr. MacDiarmid's laboratory for two weeks in order to carry out collaborative studies on polyaniline. Title of talk given: "Polyaniline: Study of the Chemical and Physical Properties as a Function of the Protonation State."
11. November 8, 1988, Dr. Bruce Parkinson, E.I. DuPont de Nemours, Wilmington, DE, met with Dr. Epstein at OSU and presented a seminar in the Department of Chemistry.
12. November 16-17, 1988, Dr. MacDiarmid gave a talk to personnel of the NSF/MRL Site Review team. Title of talk given: "Design and Synthesis of Advanced Polymers and Ceramics."
13. November 17, 1988, Dr. Epstein met at the OSU Columbus, OH, with several representatives of Historically Black Colleges and Universities to discuss current sources of funding for research in advanced materials.
14. November 23, 1988, Dr. Donald Mente and two other representatives of BASF Corporation, Wyandotte, MI, met with Dr. Epstein at OSU to discuss applications of conducting polymers.
15. November 28-December 3, 1988, Dr. Farrington presented an invited talk on solid state electrochemistry and polymer electrochemistry at the fall meeting of the Materials Research Society in Boston. Title of talk, "PEO-based Polymer Electrolytes Containing Divalent Cations."
16. November 30 - December 4, 1988, Dr. MacDiarmid attended the South West Regional ACS Meeting, Corpus-Christi, TX. Title of invited talk, "Synthetic Metals: A New Role for Organic Polymers."
17. December 6-7, 1988, Professor Carlo Taliani, Istituto di Spettroscopia Molecolare, Bologna, Italy, visited Dr. Epstein's laboratory. He met with members of Dr. Epstein's group and presented two seminars. Title of seminars presented: "Molecular Structure and Charge Transport in Polyheterocycles: Design and Properties of Low Energy Gap Conducting Polymers" and

"Photoinduced Optical Absorptions in the  $Y_1Ba_2Cu_3C_{7-8}$  Superconducting System."

18. December 9, 1988, Dr. David Mintmire, Naval Research Laboratories visited Dr. Epstein's laboratory. Title of seminar presented: "Electronic Properties of Polysilane Materials."

19. December 12-14, 1988, Dr. Epstein visited E.I. DuPont de Nemours, Wilmington, DE, to discuss joint polymer research (expenses paid by other sources).

20. December 13, 1988, Dr. Joel Miller of DuPont Research & Development Center, Wilmington, DE, visited Dr. MacDiarmid's laboratory. Title of talk given: "Organometallic Ferromagnets."

21. December 13, 1988, Dr. Teh Kuan of Lockheed Corporation, Valencia, CA, made a joint presentation with Dr. MacDiarmid to the Natural Science Association Advisory Board Meeting of the University of Pennsylvania on collaborative research between academia and industry.

22. December 14-15, 1988, Dr. MacDiarmid visited Milliken Research Corporation, Spartanburg, SC. Title of invited talk, "Chemical and Physical Properties of Polyaniline."

## V. Publications

### 1. Published Papers

#### Acknowledging URI and Other Support

##### (i) Farrington (Penn)

"Electrochemical and Stability Studies of a New Form of Polyacetylene,  $N-(CH)_x$ ," Extended Abstracts, The Electrochemical Society, 174th Meeting, Chicago, IL, October 9-14, 1988, vol 88-2, R. Huq, G.C. Farrington, J. Foreman, K. Wu and N. Theophilou. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059.)

"Solid Polymer Electrolytes:  $Zn(II)$  Mobility in Poly(ethylene oxide)," Extended Abstracts, The Electrochemical Society, 174th Meeting, Chicago, IL, October 9-14, 1988, Vol. 88-2, H. Yang and G.C. Farrington. (Supported in part by URI and in part by NSF Grants No. DMR-85-19059.)

"DMA and DSC/DETA of Poly(ethylene oxide)-Based Electrolytes," Proceedings of the 17th NATAS Conference, Lake Buena Vista, FL, October 9-12, 1988, p. 335, G.K. Jones, A.R. McGhie, R. Huq and G.C. Farrington. (Supported in part by URI and in part by NSF Grant No. DMR-85-19059.)

## 2. Papers Accepted/Submitted for Publication

### (i) Epstein and/or MacDiarmid (OSU and/or Penn)

"Reduced Interchain Spin Diffusion in Trans-Polyacetylene Due to  $sp^3$  Orbital Defects," Phys. Rev. B submitted (1988), Y.Cao, J.R. Gaines, A.J. Epstein, G.A. Arbuckle and A.G. MacDiarmid. (Supported in part by URI and in part by NSF Grants No. DMR-87-16520, DMR-86-15475, DMR-80-22870.)

"Picosecond Photoinduced Exciton Bleaching in Emeraldine Base: Crossover in Decay Mechanisms," Phys. Rev. B submitted (1988), M.G. Roe, J.M. Ginder, T.L. Gustafson, M. Angelopoulos, A.G. MacDiarmid and A.J. Epstein. (Supported in part by URI and in part by NSF Grants No. DMR-85-19059.)

"Bifurcation of Lattice Phases and Polaron Lattice/Spinless Defect Competition in Polyaniline," Phys. Rev. Lett. submitted (1988), M.E. Jozefowicz, R. Laversanne, H.H.S. Javadi, A.J. Epstein, J.P. Pouget, X. Tang and A.G. MacDiarmid. (Supported in part by URI, in part by DOE Grant No. DE-FG02-86ER 45271.A003, in part by NSF International Travel Grant No. INT-85-14202 and in part by an "Action-Initiative CNRS-NSF".)

### (ii) Farrington (Penn)

"PEO-based Polymer Electrolytes Containing Divalent Cations," Polymer Electrolyte Reviews - 2 Eds., J.R. MacCollins, C.A. Vincent, Elsevier Publishers, Switzerland, G.C. Farrington and R.G. Linford. (Supported in part by URI and in part by UK National Advisory Board Initiatives I, II & III and in part by NSF Grant No. DMR-85-19059 and in part by NATO Research Grant 86/0185.)

## VI. Patents

### Patents resulting from URI support

None

## VII. Changes in Personnel

### 1. University of Pennsylvania

#### a. Department of Chemistry (MacDiarmid)

Andrew J. Diggs was appointed as URI Project Coordinator as of October 1, 1988.

#### b. Department of Materials Science and Engineering (Farrington)

There was no change in personnel during the ninth quarter.

### 2. The Ohio State University

#### Department of Physics (Epstein)

Dr. Hamid Javadi resigned from his postdoctoral position as of October 7, 1988. He has taken a position at Los Alamos National Labs in Los Alamos, New Mexico.

Ms. Janine Bradford began employment on October 13, 1988 to assist with secretarial duties.

Keith Cromack is continuing his graduate research in Dr. Epstein's group but is no longer supported by the URI program as of December 31, 1988. He is now supported by departmental funds.

3. Lockheed Advanced Aeronautics Corporation

Aeronautics Systems Group Research (Kuan)

There was no change in personnel during the ninth quarter.

4. Rensselaer Polytechnic Institute

Department of Chemistry (Wnek)

There was no change in personnel during the ninth quarter.

5. University of Rhode Island

Department of Chemistry (Yang)

There was no change in personnel during the ninth quarter.

6. Montclair State College

Department of Chemistry (Humphrey)

There was no change in personnel during the ninth quarter.

VIII. Hiring of New Faculty from URI Funds

Funding for two new junior faculty members (each for four person-years) - one in the Department of Chemistry and one in the Department of Materials Science and Engineering - was provided in the URI contract commencing in year two.

a. Department of Chemistry (MacDiarmid)

In view of uncertainty of funding in the URI program, the School of Arts and Sciences was hesitant in proceeding immediately with a faculty search at the beginning of year 2. In fact complete funding for year 2 only became available on June 28, 1988, i.e. 8 months into year 2 i.e. 3 months before the start of year 3. When funding for year 3, which also included salaries for new

faculty became established, we were given permission to advertise and search for appropriate candidates.

The following advertisement was placed in "Chemical and Engineering News" (December 12, 1988).

"FACULTY POSITION. As part of a continuing development program, the UNIVERSITY OF PENNSYLVANIA, DEPARTMENT OF CHEMISTRY plans to add a faculty member at the assistant professor level (tenure probationary) in the general area of **materials chemistry**. The appointment could begin as early as July 1, 1989. All candidates in the general area of materials chemistry will be considered, including organic solid state and polymer chemistry, the design and synthesis of new materials and the study of their physical properties. Applicants should send a **curriculum vitae**, list of publications, description of research interests, and in addition have a minimum of three letters of recommendation sent to Amos B. Smith, III, Chairman, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323, by January 15, 1989. The University of Pennsylvania is an Affirmative Action/Equal Opportunity Employer."

In addition, ~50 letters were written to persons in the above areas requesting that they bring the above information to the attention of suitable candidates.

As of December 31, 1988, 40 applications have been received. It is expected that the new appointee will take up his position during the summer of 1989. The URI program is providing \$150,000 in startup funds for the new chemistry faculty member.

b. Department of Materials Science and Engineering (Farrington)

During the past year, the Department of Materials Science and Engineering has searched for candidates for the position of assistant professor in the area of conducting polymers, with particular emphasis on polymer physics. A number of candidates were considered and several were invited to campus. In October, the department decided to prepare a full dossier on one. In general, the letters of recommendation gathered for this person were excellent. The case was assembled and has been presented and approved by the Personnel Committee of the School of Engineering and Applied Science. It is now making its way through the formal approval process of the school and the university.



IX. Contractual Administration

1. Prime Contract - University of Pennsylvania

Funding for the third year of the contract (i.e. 10/1/88 to 9/30/89) has not been received as of 12/31/88. However, we were informed by Dr. JoAnn Milliken of ONR on December 20, 1988 that funding for the third year budget will probably involve an approximately 25% reduction. It is hoped that funding will reach the contractors by the end of February 1989.

2. Subcontractors - McGill Management, Inc.

As of September 23, 1988, the subcontract to McGill Management, Inc. was terminated. Accordingly, the services of Ms. Marie Dolton, an employee of McGill Management, were also terminated effective September 23, 1988.

X. Fiscal Status  
Expenditures and Commitments

A. University of Pennsylvania: The following represents monies spent and/or committed to that portion of the program carried on at the University of Pennsylvania.

	1 1st Year Budgeted 9/15/86-9/30/87	2 2nd Year Budgeted 10/1/87-9/30/88	3 New Funding added on 2/17/88 & 6/28/88 = <b>577,611</b>	4 Total Spent & Committed 9/15/86-12/31/88	5 Available Balance on 12/31/88	6 Budgeted Balance
U of P (Chem) (Dr. A.G. MacDiarmid)	727,044	577,611	187,466 + 390,145 = <b>577,611</b>	1,212,550	92,105	92,105†
U of P (MSE) (Dr. G.C. Farrington)	231,565	309,845	102,108 + 207,737 = <b>309,845</b>	541,410	0	0

† Available balance for MacDiarmid and Farrington consists entirely of unexpended equipment monies. These funds must be used for salaries and supplies until we have received funds for the third year budget.

B. Subcontracts

	1st Year Budgeted 9/15/86-9/30/87	2nd Year Budgeted 10/1/87-9/30/88	New Funding added on 2/17/88 & 6/28/88 = <b>369,597</b>	Total* Spent & Committed 9/15/86-12/31/88	Available Balance on 12/31/88 (1+3)-4	Budgeted Balance (1+2)-4
OSU (Dr. A.J. Epstein)	867,116	369,597	121,800 + 247,797 = <b>369,597</b>	1,236,713	0	0
Lockheed (Dr. T. Kuan)	87,037	87,037	30,732 + 56,305 = <b>87,037</b>	153,356	20,718	20,718
MM Inc. (Ms. M. Dolton)	37,143	30,246	11,985 + 18,261 = <b>30,246</b>	67,389	0	0
Academic Subcontractors a. Dr. G.E. Wnek 1. MIT 2. RPI	36,996 36,006	0 69,940	0 31,862 + 38,078 = <b>69,940</b>	36,796 82,149	200 23,797	200 23,797
b. Univ. Rhode Island (Dr. S.C. Yang)	31,862	31,862	0 + 31,862 = <b>31,862</b>	55,072	8,652	8,652
c. Montclair State (Dr. B.D. Humphrey)	29,231	31,862	14,047 + 17,815 = <b>31,862</b>	45,462	15,631	15,631

\*The following represents monies paid on receipt of demand (i.e., bills) from participating subcontractors.